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CATALYSTS FOR THE OXIDATION OF CARBON MONOXIDE AT LOW TEMPERATU--ETC(U)
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NRL Report 8353

Catalysts for the Oxidation of Carbon Monoxide at Low Temperatures

J. K. MUSICK AND F. W. WILLIAMS

Combustion and Fuels Branch
Chemistry Division

November 21, 1979

NAVAL RESEARCH LABORATORY
Washington, D.C.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

    Four catalysts (hopcalite, Whetlerite, a supported palladium, and a supported platinum) were tested for efficiency in promoting the oxidation of carbon monoxide (CO). The catalysts were tested with 3000 to 5000 ppm of CO in air at 21,000 h^{-1} space velocity, various temperatures and two relative humidities (15% and 50%).

    At room temperature and 50% RH, hopcalite has no catalytic capability and platinum has practically none. At room temperature and 15% RH, hopcalite is superior to platinum in catalyzing the oxidation of CO.

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20. Abstract (Continued)

Hopcalite is more efficient than either of the other three catalysts in the 52 to 66°C (125 to 150°F) temperature range at both humidities.

Platinum and palladium are superior to both hopcalite and Whetlerite at both humidities in the 113 to 135°C (235 to 275°F) temperature range.

Higher humidity decreases the CO-oxidizing capabilities of hopcalite and Whetlerite but does not do so for platinum and palladium.

Whetlerite is in the lower-performing group of catalysts under all except one of the different conditions used in the tests.

For the hopcalite, palladium, and platinum catalysts there is a temperature below 135°C (275°F) and above 68°C (155°F) at which CO can be oxidized efficiently.

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CATALYSTS FOR THE OXIDATION OF CARBON MONOXIDE
AT LOW TEMPERATURES

INTRODUCTION

The Navy has need for a method to remove high concentrations of carbon monoxide (CO) from enclosed atmospheres with a minimum or no use of electric power. In an emergency situation, such as a fire aboard a submarine or submersible, the CO concentration in the vessel could rise to a high level accompanied by a loss or shortage of power. The only method now available for removing CO from a ship's atmosphere without using electric power is ventilation. The normal method of CO removal is to convert it to carbon dioxide (CO_2) by passing the ship's air through a catalytic burner containing hopcalite catalyst at a temperature of about $316°C$ ($600°F$). This requires the expenditure of power. The high operating temperature for hopcalite was originally selected after it was found that at intermediate temperatures (above $100°C$) some chlorinated hydrocarbons were converted to toxic compounds [1]. Also, at these intermediate temperatures, the hopcalite adsorbed unoxidized organic compounds which could explode if the temperature of the catalyst was subsequently increased or cycled sufficiently[2]. These limitations restrict the use of hopcalite, but would not obviate its use in a crisis situation. In contrast to these hazards which prevent the routine use of hopcalite for oxidizing CO at intermediate temperatures, low catalytic activity is the reason that it is not used at room temperature. The water vapor present in submarine air at 50% RH completely destroys the activity of hopcalite for CO at room temperature [2].

Several catalysts show promise for use in a low-power low-temperature reactor to oxidize CO. The Naval Sea Systems Command (NAVSEA) requested the Naval Research Laboratory (NRL) to make a preliminary study of four of these prospective catalysts. In this study, the efficiencies of the catalysts for converting CO to CO_2 at various temperatures and humidities were measured while the studies of capacities of the catalysts, the effects of additional contaminants, and other parameters were deferred for later work. Four catalysts were investigated: (1) carbon impregnated with copper, chromium, and silver (known as Whetlerite), (2) hopcalite, (3) palladium metal, and (4) platinum metal. The program plan also included a coprecipitate of the oxides of tin (SnO_2) and copper (CUO), but a supply sufficient for the scaled burner could not be located. Time did not permit the synthesis and purification of this catalyst in a grade suitable for the burner tests. The criterion set forth as the objective of the work was to devise a method of reducing the CO concentration in an enclosed atmosphere of a volume of 4248 m^3 (150,000 ft^3) from 5000 ppm to 50 ppm and maintaining it at 50 ppm for 72 hours with a minimum or no use of electric power.

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APPARATUS

A continuing series of studies of various problems associated with the CO/H_2 burner has been conducted at NRL since before the launching of the first nuclear submarine [3]. Most of these studies involved the use of a laboratory-scale catalytic burner which was designed to reproduce, in a small catalyst bed, the conditions of contaminant concentration, pressure, temperature, linear flow velocity, and residence time which exist in the shipboard catalyst bed. The first four of these variables are readily adjustable in the laboratory burner and can be set to duplicate the conditions in the ship's burner. The fifth variable, residence time (of air in the catalyst bed) depends on both linear air velocity and the dimensions and characteristics of the catalyst bed. For this reason, the catalyst bed of the laboratory burner was made the same depth as that used in the shipboard burners. This insured that when the linear air velocity of the shipboard burner was duplicated in the laboratory burner, the residence time was simultaneously duplicated, provided that both burners were loaded with the same catalyst.

The laboratory-scale burner is a reactor with an integral preheater. Both reactor and preheater are contained in a 71-cm (28-in.) length of 2.9-cm i.d. (1-1/8 in. i.d.) stainless steel tubing mounted vertically and surrounded by two separate electrical heaters. The heaters are independently powered by two variable-voltage transformers, and the tube-heater assembly is heavily insulated with alumina-silicate fiber blanket and wrapped with glass tape. The upper section of the tube is packed with stainless steel turnings and serves as a preheater for the inlet air and the lower section contains the catalyst bed. Figure 1 is a schematic drawing of the burner. Two thermocouples are located in the burner tube; one is between the preheater and the catalyst bed and the other is at the exhaust end of the catalyst bed. The thermocouples are connected to a digital pyrometer which can be switched to display the temperature reading of either the catalyst bed inlet or exhaust air.

The burner is equipped with eight sampling lines of 0.3-cm-o.d. (1/8-in.-o.d.)n stainless steel tubing to permit sampling of the air at the burner inlet, the preheater exhaust (between the preheater and catalyst bed), at 2.5-cm (1-in.) increments of catalyst bed depth, and at the burner exhaust. The bed-sampling tubes are welded to the burner tube and have 0.2-cm-o.d. (0.072-in.-o.d.) extensions with square-cut ends which project 1 cm (3/8 in.) into the catalyst bed. The inlet and exhaust sampling tubes are attached to the burner inlet and exhaust lines with tube fittings and do not project into the airstream. The sampling tubes are made about 1.2 m (4 ft) long to provide cooling for the gas samples and are connected through stainless steel toggle valves to a gas chromatograph. These provisions for sampling and analyzing the burner air stream at successive 2.5-cm (1-in.) increments of catalyst bed depth make it possible to follow very closely the reactions which take place in the catalyst bed.
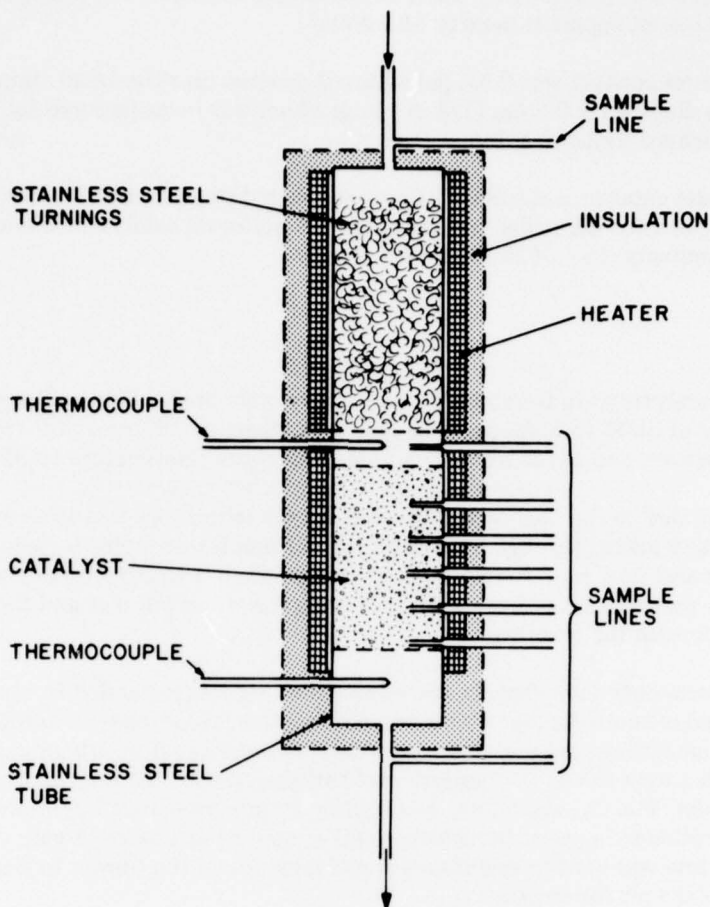
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Fig. 1 — Laboratory-scale catalytic burner

CATALYSTS

Whetlerite is a coal-based activated charcoal impregnated with silver, copper, and chromium from an ammoniacal solution and then dried. It is called Whetlerite after J. C. Whetzel and E. W. Fuller who were instrumental in its development. The material used in these tests had a mesh size of 12-30 and was made at NRL under the military specification, "Charcoal, Activated, Impregnated, Type ASC," MIL-C-19008 (ships).

The hopcalite catalyst was manufactured by the Mine Safety Appliances Corporation and was purchased through Navy supply channels on the military specification, MIL-C-21665 (ships), 12 December 1958, amended 11 May 1959. It is a coprecipitate of copper and manganese oxides which has been analyzed as 78.3 wt-% MnO_2 and 13.1 wt-% CuO with

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a 7 9 wt % ignition loss (presumably water or chemisorbed gases). The catalyst is about 6 mesh size and has an apparent density of 1 g/cm^3.

The palladium catalyst was 0 5% palladium deposited on cylindrical alumina pellets 0.3 cm (1/8 in.) diameter x 0.3 cm (1/8 in.) long which was manufactured by the Chemical Division of Englehard Industries Inc.

The platinum catalyst was 0.3% platinum deposited on cylindrical alumina pellets similar to those used for the palladium catalyst. The platinum catalyst was manufactured by the Baker Company Inc. of Newark, New Jersey.

PROCEDURE

The four catalysts were tested in the laboratory-scale burner using CO concentrations in the burner air of 3000 to 5000 ppm, relative humidities of 15% and 50% (measured at room temperature) and temperatures varying from room temperature to 327°C (620°F).

The air supplied to the burner was taken from the laboratory 621-kPa (90-psi) compressed air line and passed through a pressure regulator and flowmeter for adjustment to the desired pressure and flow rate. In experiments using 50%-RH air, the humidity was adjusted to that value by passing part of the air stream through a water bubbler and then recombining and mixing it with the main stream.

In the experiments using dry air, the compressed air was expanded to atmospheric pressure and used without further treatment. This dry air had a relative humidity of about 15%. After the air stream was adjusted to the desired pressure, flow rate, and humidity, it was contaminated with CO to the desired level and then passed through a mixing loop and to the burner inlet. The CO was added by bleeding from a pressurized cylinder with the flow rate being controlled by a pressure regulator and a small needle valve. A gate valve at the burner exhaust line was used to maintain a slight pressure on the burner to permit easy leak-free sampling of the air for analyses.

An air flow of 4.7 by 10^{-4} m^3/s (1 cfm) was passed through the catalyst bed which has a 6.5-cm^2 (1-$in.^2$) cross-sectional area and a 12.7-cm (5-in.) depth. This provided a space velocity of 21,000 h^{-1} which duplicates that of the shipboard catalyst bed.

Samples of burner air were taken at 2.5-cm (1-in.) increments of the catalyst bed depth and analyzed by gas chromatography. The analytical results were used to calculate catalyst efficiencies and contaminant decay rate curves to compare the characteristics of the catalysts. In a few tests in which the activity was very low, the concentrations of CO at increments of bed depth were not made. Instead of making incremental analyses in those cases, only the changes taking place in the entire bed were measured.

In some tests, it was difficult to maintain both burner inlet and exhaust at the same temperature. One reason for this was that heat was generated by the combustion of the CO entering the burner. For example, in a room temperature test of hopcalite when no power was being supplied to the burner, the temperature of the gas stream was increased by about

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11°C (20°F) while passing through the burner. Similarly, the exhaust temperature ran higher than the inlet in some low temperature runs when power was being applied only to the preheater and not to the catalyst bed. Both inlet and exhaust temperatures were relatively constant after equilibrium was attained, even in those tests where the inlet temperature was 11°C (20°F) lower than the exhaust temperature. In no test was the inlet temperature higher than the exhaust.

ANALYSES

High concentrations of CO (about 100 ppm and higher) were measured with a Hewlett-Packard 5710A gas chromatograph using a thermal conductivity detector with a 0.9-m by 0.3-cm (3 ft by 1/8-in.) stainless steel column of 70/80 mesh Type 5A molecular sieve at 55°C.

Low concentrations of CO (about 1 to a few hundred ppm) were measured with a GC-2A gas chromatograph which had been modified to analyze CO and CO_2 in the parts-per-million range. In the modified instrument, the gas sample to be analyzed was first passed through a chromatographic separation column containing equal weights of Porapak Q and Porapak T to separate the CO_2 which interferes with the CO analysis. The CO_2 was removed by backflushing, and the sample then passed through a column of Type 5A molecular sieve, which separated the CO from any methane (CH_4) which might have been in the air. From the molecular sieve column, the sample passed with a stream of hydrogen to a reactor (a bed of 10%-Ni on Chromosorb W at 320 to 340°C), which converted the CO to CH_4. Next, the sample passed to the hydrogen-flame ionization detector where the original CH_4 and the CH_4 formed from CO were detected as separate peaks. Both the Porapak and molecular sieve columns were maintained at 65°C [4].

Air samples from the burner were delivered to both chromatographs by toggle valves through 0.3-cm-o.d. (1/8-in.-o.d.) stainless steel sampling lines. The chromatographs were interfaced with an integrator and computer which calculated and read out the results on a teletype.

RESULTS

Method of Presentation

The results are presented in two tables and 12 figures (2, 3, and 5 through 14). The figures show various curves which describe the performances the catalysts would provide if they were used in a full-size burner aboard a typical submarine. Each curve shows the decrease with time of the concentration of CO produced by the operation of one burner (using a particular catalyst and particular operating conditions) in a submarine atmosphere. To determine the coordinates of these curves, the CO-removal efficiency of each catalyst studied was evaluated in the laboratory-scale catalytic burner as described in the preceding discussion. The efficiencies thus determined were expressed as fractions of the inlet CO concentrations oxidized by the catalyst beds. The conversion from measured laboratory

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performance of a catalyst to calculated shipboard performance was made by the use of the first-order decay law. In this equation,

$$\log C = 3.7 - \frac{tA}{698}$$

where C is the concentration of CO in the submarine's atmosphere in ppm, t is the time in minutes from the start-up of the shipboard catalytic burner, and A is the fraction of CO entering the burner which is oxidized by the burner (measured in the laboratory).

The equation is based on the assumptions that a submarine of 4250 m^3 $(150,000 \text{ ft}^3)$ of floodable volume is contaminated with 5000 ppm of CO and that a catalytic burner handling $0.24 \text{ m}^3/\text{s}$ $(500 \text{ ft}^3/\text{min})$ of the submarine's air removes the fraction A of the CO entering the burner. Derivation of the equation is given in the Appendix.

In cases where 100% of the CO is oxidized, the equation makes no distinction between a very active catalyst which uses only a fraction of its bed and a less active catalyst which requires 100% of its bed to carry out the oxidation. For this reason, some of the following comparisons of catalyst performances are based on fractional portions of the standard 12.7-cm-thick (5-in.-thick) catalyst bed.

The results of the laboratory tests are summarized in Table 1. These results are converted by the method described above to the theoretical shipboard performance curves shown in the figures in this report. The temperatures reported for these curves are average exhaust temperatures. Exhaust temperatures did not vary more than a few degrees during a test (after equilibrium was reached) and, being the highest temperatures in the burner, are presumed to be the controlling temperatures for the oxidations.

The concentration of CO in the burner air supply varied quite widely in some of the early tests, and for each of these tests the ranges of concentrations are listed in Table 1. In later tests, an improved technique made it possible to control the inlet CO concentration more accurately and the measured concentration in each of these tests is expressed as a single value. In those tests for which a single figure is tabulated, the measured CO concentrations were within ± 100 ppm of that figure.

The sampling lines installed at 2.5-cm (1-in.) intervals in the laboratory burner described above permitted analyses of the burner air to be made at 20%-increments of the catalyst bed depth. With this information available, it was possible to tabulate in Table 1 the proportion of the inlet CO removed by a particular percentage of the catalyst bed. Thus, if the table shows that 50% of the influent CO was oxidized by 20% of the catalyst bed, then the other 50% of the CO was oxidized by the second 20%-increment of catalyst, giving 100% oxidation of the CO while leaving 60% of the catalyst bed unused.

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Table 1 -- Summary of Results

Test No.	Humidity (%RH)	Av Exh. Temp.		Inlet CO Con. (ppm)	Proportion of Inlet CO Removed (%)	Proportion of Catalyst Bed Utilized (%)
		(°F)	(°C)			
Hopcalite						
320	50	615	324	4000-9000	99.7	20
321	50	620	327	5000-7000	99.7	20
324	50	235	113	3500-5000	100	60
325	50	240	116	3500-5000	100	100
327	50	135	57	3500-5000	50	100
328	15	150	66	4500	90	100
329	15	140	60	3500-4500	65	100
330	15	90	32	3300	45	100
331	50	75	24	3000	0	100
Whetlerite						
333	50	125	52	3000	0	100
333	50	235	113	3000	20	100
334	15	130	54	3100	5	100
334	15	250	121	3100	93	100
335	15	355	179	3100	93	40
336	50	360	182	2900	96	60
Palladium						
337	50	485	252	3500	100	20
338	50	145	63	4700	26	100
339	50	270	132	4600	85	20
340	15	145	63	4900	4	100
341	15	270	132	4900	85	20
Platinum						
343	50	75	24	4900	1	100
343	15	75	24	5100	0.2	100
344	50	270	132	5200	95	20
345	50	150	66	4900	4	100
346	15	150	66	4900	2	100
347	15	155	68	5300	2	100
347	15	275	135	5100	80	20

Hopcalite

The performance of hopcalite in oxidizing CO in humid air (50% RH) is shown in both Table 1 and Fig. 2. The lowest of the three curves in Fig. 2 represents complete oxidation of all the CO entering the burner. This result was obtained in the laboratory in the temperature ranges of 324 to 327°C (615 to 620°F) and 113 to 116°C (235 to 240°F) and would presumably be true of any temperature above the lower range. At 324 to 327°C (615 to 620°F) only a fraction of the catalyst bed was required to oxidize the CO. As can be seen in Table 1, almost all the influent CO was oxidized by 20% of the catalyst bed. The middle curve of Fig. 2 shows the performance of hopcalite at a temperature of 57°C (135°F). In this case, the hopcalite oxidized only 50% of the influent CO. The top curve represents hopcalite's performance at room temperature and shows that there was no measurable oxidation of the CO.
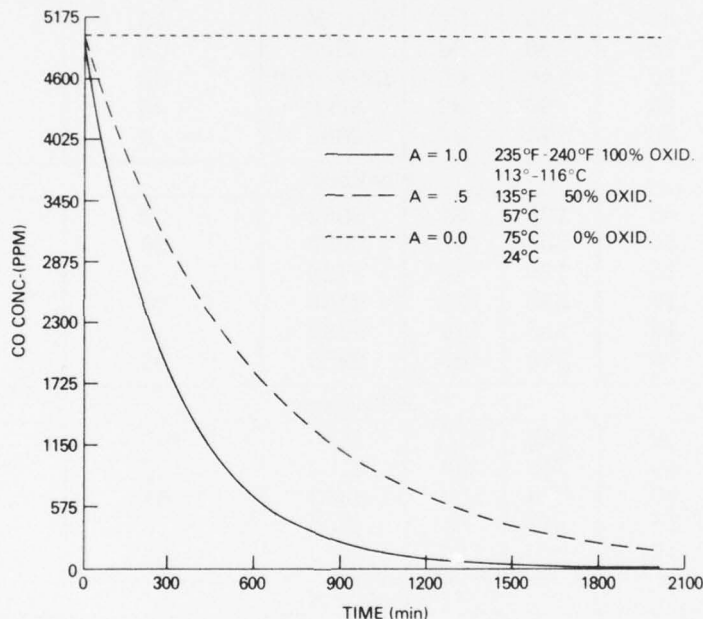

Fig. 2. — Performance of hopcalite—concentration of CO for
50%-RH at various temperatures

The data in Table 1 show the performance of hopcalite in relatively dry (15% RH at room temperature) air and the CO-decay curves for these tests are shown in Fig. 3. Here it is seen that the catalyst is much more efficient when used in 15%-RH air than it is when exposed to 50%-RH air. Even at room temperature, 45% of the inlet CO is oxidized in the dry air. This is shown by the 32°C (90°F) – curve. In this test, no heat was applied to the catalyst but the heat of oxidation of the CO raised the temperature of the burner air from 22°C (72°F) at the burner inlet to 32°C (90°F) at the exhaust. In the two other tests of
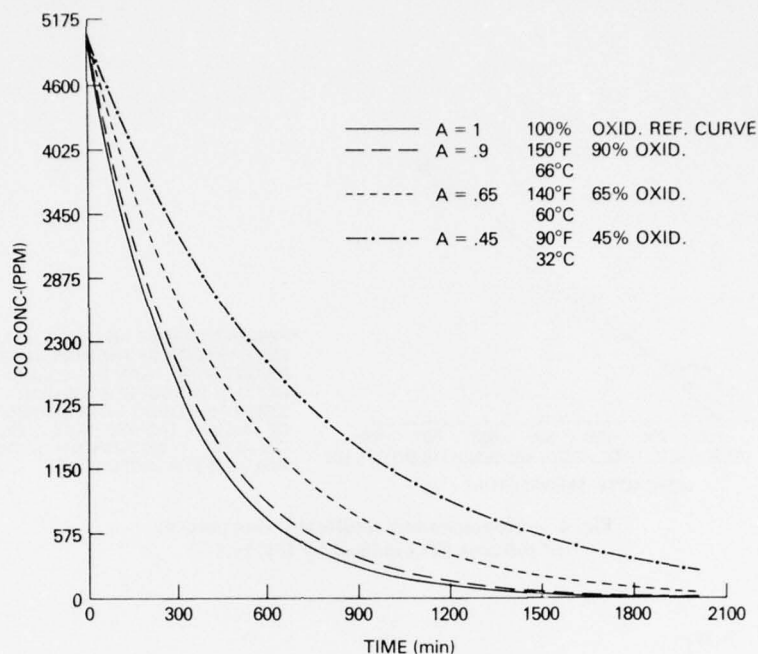
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Fig. 3 — Performance of hopcalite — concentration of CO for
15%-RH air at various temperatures

hopcalite in the 15%-RH air, the measurements were 65% of the influent CO oxidized at
60°C (140°F) and 90% oxidized at 66°C (150°F). This 25% increase in the degree of oxida-
tion is a little more than would be expected for the 6°C (10°F) increase in temperature.
It can be seen in Fig. 4 that a 10% increase in degree of oxidation would be expected.
Fig. 4 is a plot of the percent of the influent CO oxidized vs. the temperature in °F for all
of the hopcalite tests. Possibly, part of this 25% increase is due to experimental error. The
lowest curve in Fig. 3 is for comparison and shows the decrease in CO concentration
resulting when the burner oxidizes 100% of the influent CO.

In Fig. 5, the performances of separate 2.5-cm (1-in.) increments of catalyst bed are
shown for the test made with air at 50% RH and 113°C (235°F) temperature. Equal incre-
ments of the catalyst bed should give identical performances and a specific thickness of bed
should provide the same performance when it is part of a thicker bed as it does when used
separately as a complete bed. The curves of Fig. 5 show that the first inch (20%) of the
catalyst bed oxidized 36% of the influent CO while the second inch oxidized 39%. The
remaining CO was oxidized on the third 1-inch increment of the catalyst bed. Therefore the
decay curve for 60% (or any higher percentage) of the bed is the same as the one for the full
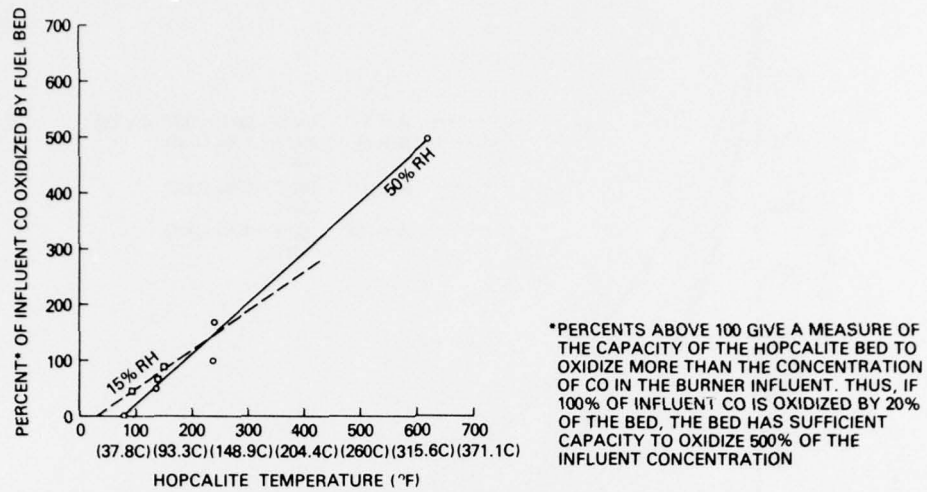bed.

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Fig. 4 — Hopcalite test results showing percent
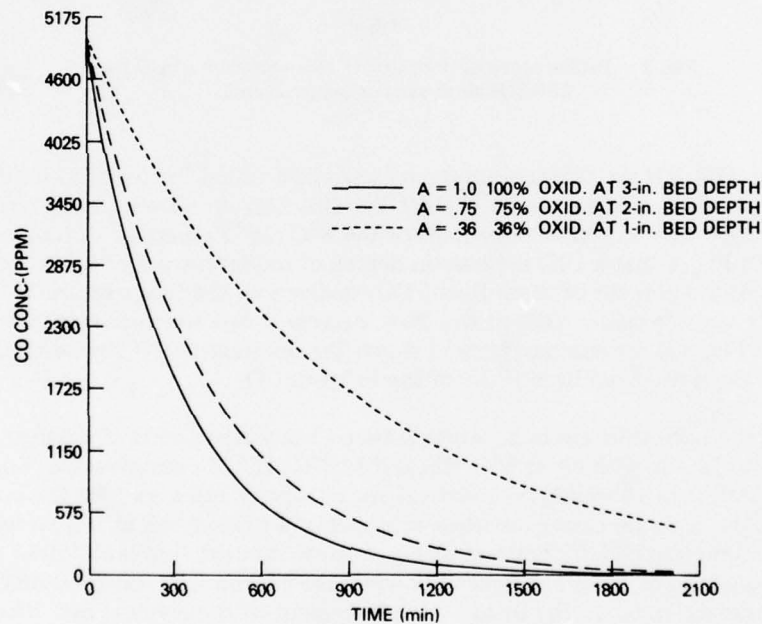of influent CO oxidized by fuel bed

Fig. 5 — Performances of hopcalite/catalyst bed increments at
50%-RH air

Whetlerite

The test results of Whetlerite catalyst are tabulated in Table 1 and converted to the CO decay curves shown in Figs. 6, 7, and 8. The curves in Figure 6 describe its performance in 50%-RH air.
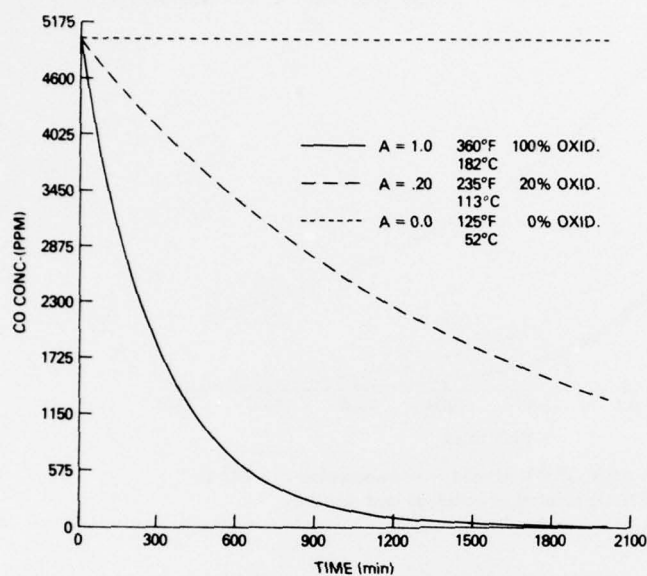

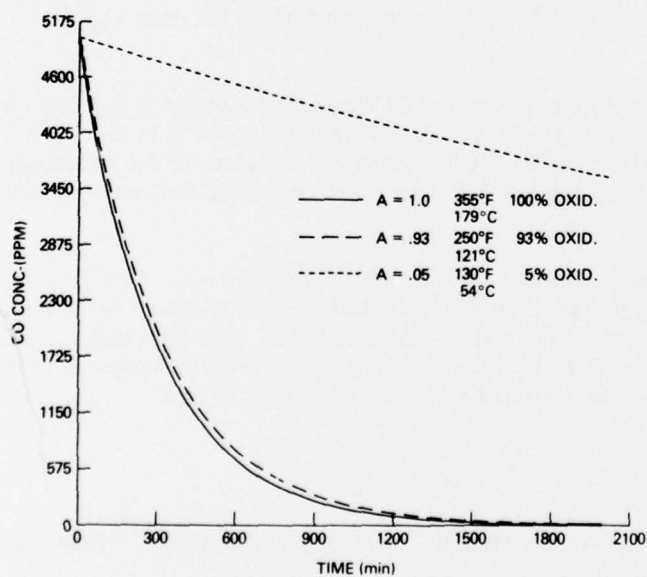Fig. 6 — Performance of Whetlerite — concentration of CO at 50%-RH air

Fig. 7 — Performance of Whetlerite —concentration of CO at 15%-RH air
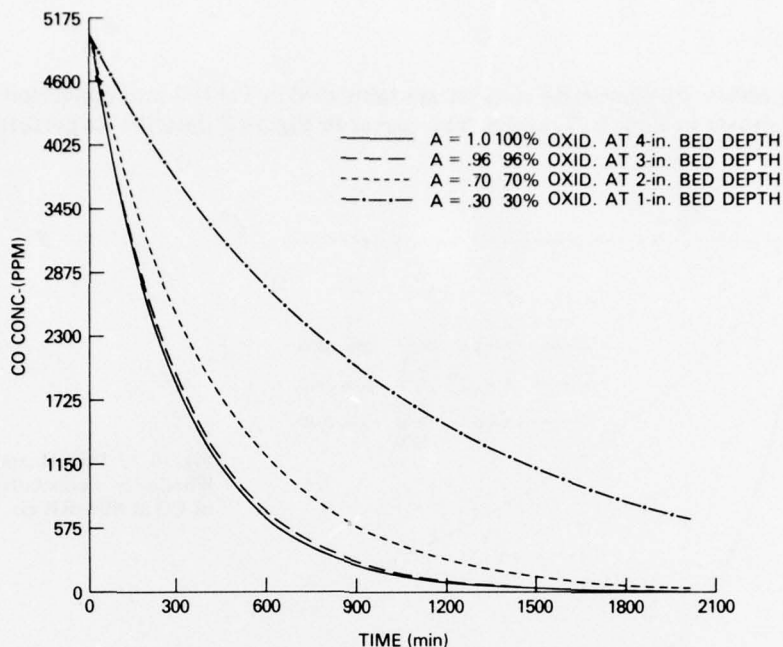
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Fig. 8 — Performance of Whetlerite — concentration of CO at
50%-RH air at various catalyst bed depths

Although no CO is oxidized at 52°C (125°F), 20% reacts at 113°C (235°F), and 100%
is oxidized by less than 80% of the catalyst bed at 182°C (360°F). Thus, to oxidize the CO
efficiently, it is necessary to heat the Whetlerite to some temperature between 113°C
(235°F) and 182°C (360°F).

As was the case with hopcalite, the performance of Whetlerite is better at low humidity
than at high. In air at 15% RH, 5% of the influent CO was oxidized at 54°C (130°F), 93% at
121°C (250°F), and 100% at 179°C (355°F). At the latter temperature, all the oxidation
was effected within 60% or less of the catalyst bed. The curves for these 15%-RH tests are
shown in Fig. 7.

The performances of various thicknesses of Whetlerite catalyst bed in 50%-RH air and
182°C (360°F) are shown in Fig. 8. The first inch (20%) of the bed removed 30% of the
influent CO, the second inch removed 40%, and the third inch 26%. The remaining 4% of the
influent CO was removed in the fourth inch of the bed. Therefore, the CO decay curve for
3 inches (60%) of the bed is very close to that for 4 inches (80%) of the bed.

Palladium

The tests of the palladium catalyst are tabulated in Table 1 and described by the CO-
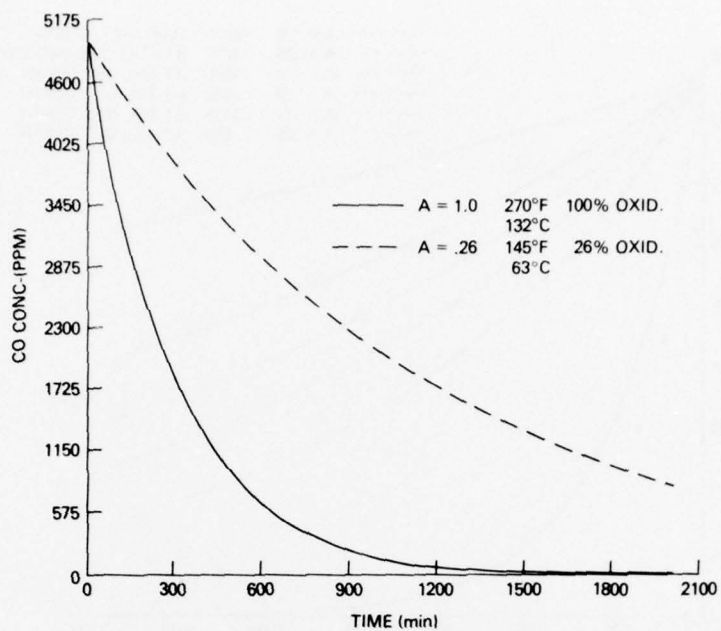decay curves in Figs. 9 to 11.

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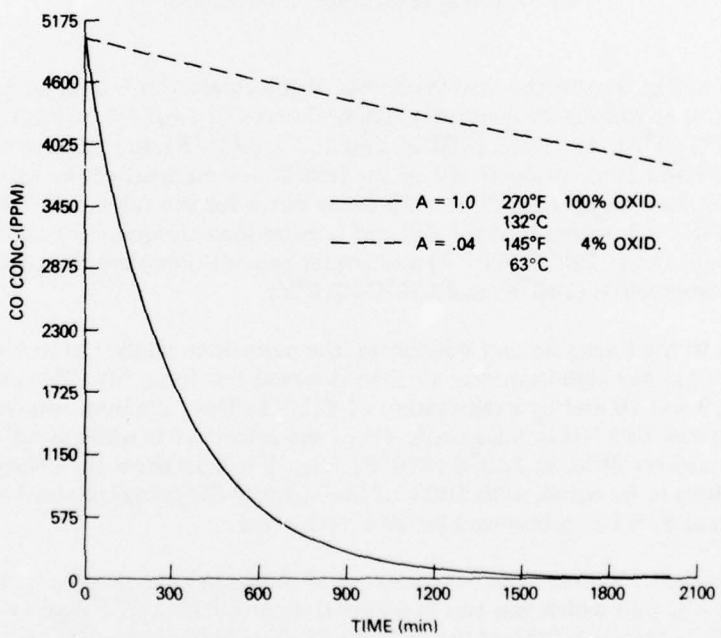Fig. 9 — Performance of palladium—concentration of CO at
50%-RH air

Fig. 10 — Performance of palladium—concentration of CO at
15%-RH air

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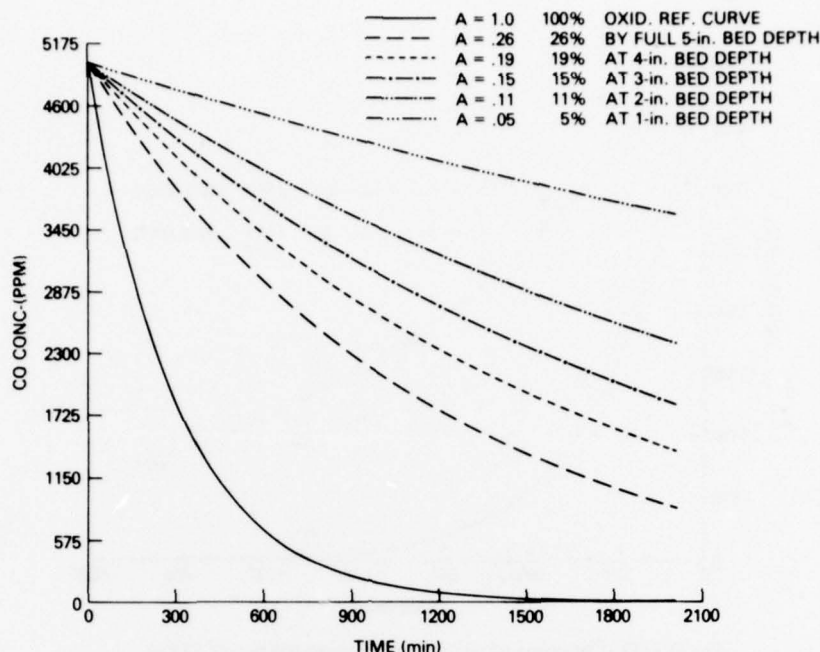|	A = 1.0	100%	OXID. REF. CURVE
	A = .26	26%	BY FULL 5-in. BED DEPTH
	A = .19	19%	AT 4-in. BED DEPTH
	A = .15	15%	AT 3-in. BED DEPTH
	A = .11	11%	AT 2-in. BED DEPTH
	A = .05	5%	AT 1-in. BED DEPTH

Fig. 11 — Performance of palladium—concentration of CO at
50%-RH air at various catalyst bed depths

The curves in Fig. 9 show the results of tests of the catalyst in humid air (50% RH at room temperature) at various temperatures. The influent CO was 26% oxidized by the catalyst at 63°C (145°F). At 132°C (270°F) and 252°C (485°F), the CO was oxidized to the extent of 85% and 100% respectively by the first 20%-increment of the catalyst bed. Thus, for both of these temperatures, the CO decay curve for the full catalyst bed is on the 100%-oxidized line. This shows that the full bed is more than adequate for complete oxidation of the influent CO at 132°C (270°F) and would provide complete oxidation at some temperature between 63°C (145°F) and 132°C (270°F).

In contrast to the hopcalite and Whetlerite, the palladium catalyst at low temperature was more efficient in the high-humidity air than it was at low humidity. This can be seen by comparing Figs. 9 and 10 and by examination of Table 1. The palladium catalyst operating at 63°C (145°F) and 15% RH oxidizes only 4% of the influent CO while at 63°C (145°F) and 50% RH it oxidizes 26%. At 132°C (270°F), Figs. 9 and 10 show the efficiencies at low and high humidities to be equal, with 100% of the influent CO being oxidized in both cases by the full bed and 85% being removed by 20% of the bed.

The efficiencies of 2.5-cm (1-in.) increments of the palladium catalyst bed were measured in test No. 338 which was run in 50%-RH air at 63°C (145°F). The results are shown in Fig. 11. In this test, 26% of the influent CO was oxidized by the 12.7-cm-thick (5-in.-thick) catalyst bed and it would be expected that each 2.5-cm (1-in.) increment of the bed would oxidize the same amount of CO. The actual measurements for the different

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increments were 5%, 6%, 4%, 4%, and 7%. The variation of these numbers from the average is probably due to experimental error. The 100% oxidation line is included in Fig. 11 for reference.

Platinum

The results of tests of the platinum catalyst are summarized in Table 1 and the CO-decay curves based on that data are plotted in Figures 12 to 14. Referring to Table 1, it is seen that the platinum catalyst was tested at three different temperatures in both the high and low humidity air. The 50%-RH decay curves are plotted in Fig. 12 and the 15%-RH curves in Fig. 13. In the 50%-RH air, the platinum catalyst oxidized 1% of the influent CO at $24°C$ ($75°F$), 4% at $66°C$ ($150°F$) and 95% in only 20% of the catalyst bed at $132°C$ ($270°F$). In the 15%-RH air, it oxidized 0.2% of the influent CO at $24°C$ ($75°F$), 2% at $66°C$ ($150°F$) and 80% in 20% of the catalyst bed at $135°C$ ($275°F$). In 15%-RH air, as in 50%-RH air, there is an intermediate temperature between $66°C$ ($150°F$) and $135°C$ ($275°F$) at which 100% of the influent CO will be oxidized and 100% of the catalyst's bed utilized.
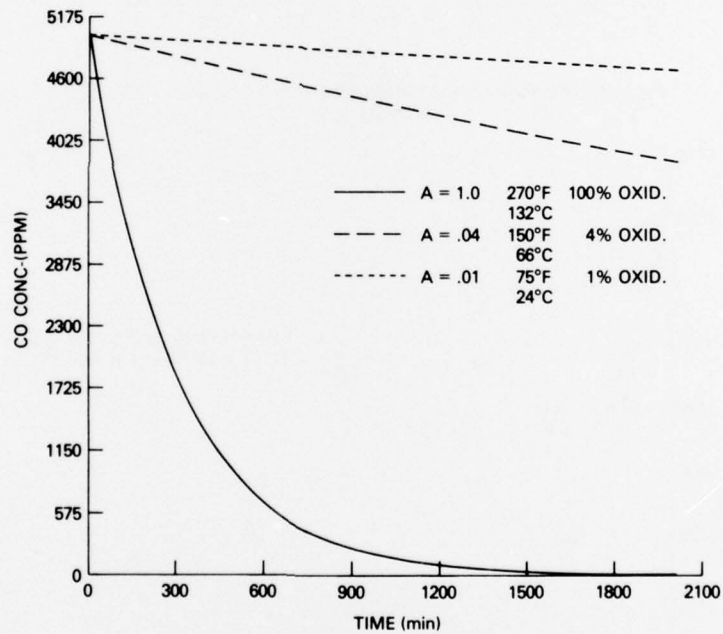

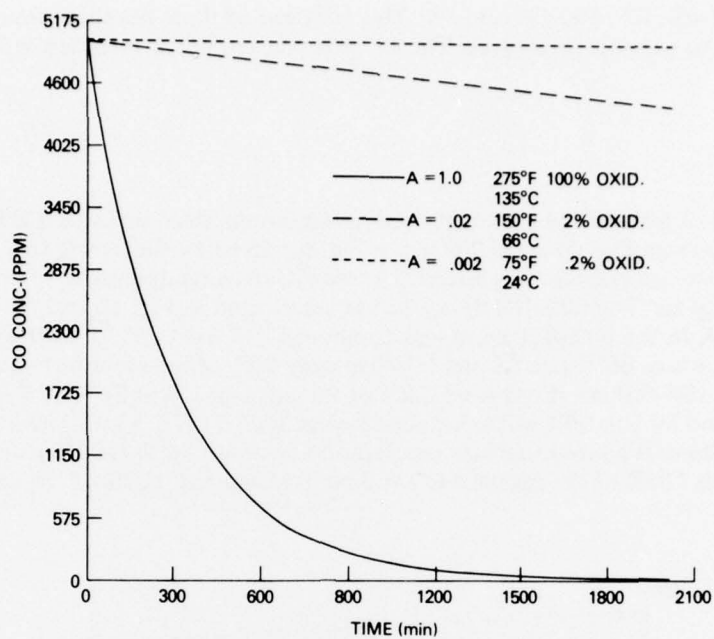Fig. 12 — Performance of platinum—concentration of CO at
50%-RH air

Fig. 13 — Performance of platinum—concentration of CO at
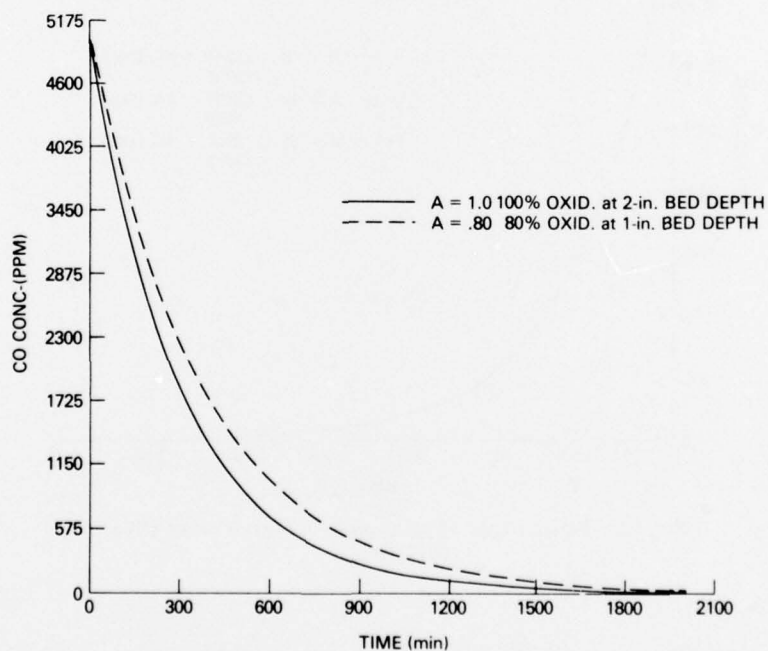15%-RH air

Fig. 14 — Performance of platinum—concentration of CO at
15%-RH air at various catalyst bed depths

These results indicate that the efficiency of the platinum catalyst is slightly higher in the high-humidity air than it is in the low-humidity air. This behavior is similar to that observed in tests of the palladium catalyst but is the opposite of that observed for the hopcalite and Whetlerite.

The curves in Fig. 14 are the CO-decay curves for successive 2.5-cm (1-in.) increments of the platinum catalyst bed (based on Test 347 in Table 1). The first inch of catalyst oxidized 80% of the influent CO and is represented by the higher curve in the figure. At succeeding 2.5-cm (1-inch) depths of the catalyst bed, the CO had been 100% oxidized and all of these catalyst bed thicknesses are represented by the 100%-oxidized curve.

Catalyst Comparison

A comparison of the performances of the four catalysts under different conditions of temperature and humidity is presented in Table 2. Data in the first line of Table 2 compare the performances of the catalysts in air at 113°C (235°F) to 132°C (270°F) and 50% RH. Due to the high reactivity of the catalysts under these conditions, the comparisons are made on the basis of catalyst beds having 20% the thickness of the beds in the shipboard burner. The tests showed the efficiency of the catalysts to be as follows: platinum (95% of CO oxidized), palladium (85% oxidized), hopcalite (20% to 33% oxidized) and Whetlerite (4% oxidized). The two values for hopcalite, 20% and 33% oxidized, were measured in two different tests and hopcalite apparently lost some of its activity in the period between the tests. This does not ordinarily happen when hopcalite is used at 316°C (600°F) unless it is exposed to certain poisons such as sulfur compounds. Since in the present case the hopcalite was used at a lower temperature, additional testing would be required in order to determine whether its activity really changed to such an extent. The platinum and palladium catalysts were tested at 132°C (270°F) while the hopcalite and Whetlerite were tested at 113 to 116°C (235 to 240°F) and this temperature difference accounts for some of the difference in activity of the catalysts. However, by plotting the percent of CO oxidized vs temperature for all the tests of the hopcalite and Whetlerite catalysts as shown in Fig. 4 and interpolating to determine the percent CO that would be oxidized at 132°C (270°F), it was found that the difference in temperature accounted for only about half of the difference in activity. Therefore, the order in which the four catalysts are listed above (from most active to least active) is correct, even though the platinum and palladium catalysts have some advantage from being tested at a higher temperature.

Table 2—Comparison of Catalysts

Temperature		Relative Humidity	Depth of Catalyst Bed Used	Percent of Influent CO Oxidized by Catalyst			
(°F)	(°C)	(%)	(%)	Hopcalite	Whetlerite	Palladium	Platinum
235-270	113-132	50	20	20-33	4	85	95
125-150	52- 66	50	100	50	0	26	4
250-275	121-135	15	20	—	19	85	80
130-150	54- 66	15	100	65-90	5	4	2

The performances of the four catalysts in the temperature range of 52 to 66°C (125 to 150°F) and with air at 50% RH is shown in the second line of Table 2. Under these conditions the catalysts were found to have the following activities: hopcalite (50% of influent CO oxidized), palladium (26% oxidized), platinum (4% oxidized) and Whetlerite (0% oxidized). It is to be noted that hopcalite is the most efficient catalyst at 52 to 66°C (125 to 150°F) whereas platinum and palladium were first and second best at 132°C (270°F).

In the third line of Table 2 the CO removal performances of the catalysts for the conditions of 121 to 135°C (250 to 275°F) and 15% RH are shown. Due to the high reactivity of the catalysts at these conditions, the curves are based on the action of a catalyst bed only 20% as thick as the shipboard catalyst bed. The results show that 85% of the influent CO was oxidized by the palladium catalyst, 80% by the platinum and 19% by the Whetlerite. There are no data for hopcalite in this temperature and humidity range, but interpolating from the other data indicates that hopcalite would oxidize about 40% of the influent CO under these conditions. This figure would place it in the third position having less activity than palladium and platinum and more Whetlerite. This is the same relative position it occupied when tested at 113 to 132°C (235 to 270°F) and 50% RH, as shown in the first line of the table.

For the conditions of 54 to 66°C (130 to 150°F) and 15% RH, the performances of the four catalysts are shown in the fourth line of Table 2. The results show 65-90% of the influent CO oxidized by the hopcalite, 5% by Whetlerite, 4% by palladium and 2% by platinum. As can be seen in Table 1, the hopcalite test resulting in 65% oxidation was run at a temperature 6°C (10°F) lower than was the test resulting in 90% oxidation. Referring again to the temperature vs percent oxidized curve of all similar tests, (Fig. 4) it is seen that the 6°C (10°F) difference in test temperatures does not account for all of the change in activity from 90% to 65% oxidized. Apparently there was some decrease in the activity of the hopcalite prior to the latter test.

The hopcalite and platinum catalysts were tested at room temperature in the both 15% and 50%-RH air. The hopcalite oxidized 45% of the influent CO in the 15%-RH air but 0% in the 50%-RH air. The platinum catalyst oxidized 0.2% of the CO in the 15%-RH air and 1% in the 50%-RH air.

Conclusions

Some conclusions which can be drawn from the comparisons of the performances of these catalysts are:

- The platinum and palladium catalysts were more efficient than either the hopcalite or Whetlerite at both humidities in the 113°C (235°F) to 135°C (275°F) temperature range.

- Hopcalite was more efficient than either of the other three catalysts at both humidities in the 52°C (125°F) to 66°C (150°F) temperature range.

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- Hopcalite is superior to platinum in oxidizing CO at room temperature and 15% RH. At room temperature and 50% RH, hopcalite has no capability and platinum oxidizes only 1% of the influent CO.

- Higher humidity decreases the CO-oxidizing capabilities of hopcalite and Whetlerite but does not do so for the platinum and palladium.

- Whetlerite was in the lower performing group in all the different sets of conditions tested except at 15% RH and 54 to 66°C (130 to 150°F). Under these conditions, it performed as well or better than the platinum and palladium.

DISCUSSION

Solely on the basis of carbon monoxide oxidizing efficiency and without regard to other important parameters which have not yet been investigated, none of the four catalysts studied is suitable for submarine use at room temperature. In the 52 to 66°C (125 to 150°F) temperature range, hopcalite is the best catalyst of the four, oxidizing 50% of the influent CO in 50% RH air or 65-90% in 15%-RH air. At temperatures of 113 to 135°C (235 to 275°F) all of the catalysts except Whetlerite oxidize 100% of the influent CO when in 50%-RH air. Platinum and palladium do this in less than 40% of the bed while hopcalite requires 60% or more. In view of these results, temperatures below 135°C (275°F) and above 68°C (155°F) might be selected which would result in both 100% oxidation of the CO and 100% utilization of the catalyst bed for all three catalysts.

Jagow et al. [5] found that residence times of between 0.2 and 0.5 seconds result in 100% conversion of CO at room temperature for 0.5% platinum on alumina, 0.5% palladium on alumina, 2% palladium on alumina, and 2% platinum on 4 to 8-mesh carbon. Further, they found that residence times of 5 seconds for hopcalite at 38°C (100°F) and 0.35 second for hopcalite at 60°C (140°F) produced 100% conversion of CO. They noted that room temperature hopcalite did not promote 100% conversion, even at high contact times, after a sufficient period of time to allow the hopcalite to absorb moisture from the air stream. The 21,000-hour[-1] space velocity used in the tests covered by this report is equivalent to 0.17 second residence time.

The hopcalite, palladium and platinum catalysts should be further tested in the temperature range of 68°C (155°F) to 135°C (275°F) and in the presence of expected atmospheric contaminants to more accurately define their capability. It appears that they will not be suitable for use at room temperature. It is known that there are some problems associated with the use of hopcalite in this temperature range, but this may not be true of the palladium and platinum catalysts. Further, some catalyst more suitable than either of the four studied might be found or developed. However, Jagow et al. [5] concluded that noble metals and mixed metal oxides were the only catalysts that hold promise for carbon monoxide oxidation at temperatures below 60°C (140°F).

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Appendix

CALCULATION OF DECAY RATE OF CARBON MONOXIDE
IN AN ENCLOSED SPACE

1. Once the immediate threat of a fire in an enclosed, self-sufficient environment has been countered, it next becomes imperative to revitalize the atmosphere in a timely fashion. During a fire of any magnitude, three major gas concentrations in the atmosphere will be altered: oxygen (O_2), carbon dioxide (CO_2), and carbon monoxide (CO). This calculation deals with the removal of high concentrations of CO with existing shipboard equipment.

2. The concentration of CO that was chosen for this calculation was taken from confined space fire tests [A1-A8]. The burner efficiency of 100% was taken from previous CO/H_2 hopcalite burner studies [A1-A8] and the following assumptions were made:

    ● There is rapid gas mixing in the enclosed space. This would be true if ventilation power were available.

    ● There is no further generation of carbon monoxide. This would be the case if the fire were *completely extinguished*. (It would not be difficult, though, to put a carbon monoxide generation term in the calculation below).

    ● There is no air exchange with the outside environment.

    ● There is no burner by-pass (channeling) in the catalyst bed.

3. The equation that has been developed to evaluate the CO concentration with time is:

$$\text{Rate of Change of CO conc. in submarine} = -\ \text{Rate of oxidation of CO in burner} + \text{Rate of input of CO from extraneous sources (fire).}$$

Since we made the assumption that the fire was extinguished, the last term is eliminated; therefore

$$d[CO] = -\ K\ [CO]_0\ dt,$$

where

$[CO]$ = concentration of CO in the submarine at time t,

$[CO]_0$ = concentration of CO in the submarine at time, 0 (5000 ppm = 5725 mg/m^3),

t = time in minutes,

K = specific rate constant for oxidation of CO by the burner

$$= \frac{FA}{V} = \frac{(500 \frac{ft^3}{min})(1.00)}{150,000 \ ft^3} = 0.0033 \ min^{-1},$$

F = Gas flow through the burner $\approx 500 \frac{ft^3}{min} = 14.16 \frac{m^3}{min} = 850 \frac{m^3}{h}$,

A = Fraction of influent CO oxidized in the burner = 1.00,

V = Submarine's floodable volume = 150,000 ft^3 = 4250 m^3.

Integrating the equation,

$$\int d[CO] = -K \int [CO]_0 \ dt,$$

$$\int_{t_0}^{t} dt = -\frac{1}{K} \int_{[CO]_0}^{[CO]} d \frac{[CO]}{[CO]_0},$$

$$t \Big|_{t_0}^{t} = -\frac{1}{K} \ln [CO] \Big|_{[CO]_0}^{[CO]},$$

$$t - t_0 = -\frac{2.303}{K} (\log [CO] - \log [CO]_0).$$

Since $t_0 = 0$,

$$t = -\frac{2.303}{0.0033} (\log [CO] - \log 5000),$$

$$\frac{t}{698} = -\log [CO] + 3.7,$$

$$\log [CO] = 3.7 - \frac{t}{698}.$$

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4. Using this equation, the variation of the carbon monoxide concentration with time can be evaluated. A plot of the equation is shown in Fig. A1. Also shown are some physiological effects that could be expected at various workloads and CO concentrations (reference [A8]). For men to survive in this environment, it is assumed that an auxiliary supply of air will be available for a period of time. The calculation shows that with two burners it would require 8 hours to reduce the CO to 200 ppm and with one burner it would require 16 hours. Reference ([A8] indicates that at this concentration a person's carboxyhemoglobin would be at 10% after 30 minutes of heavy work. This exposure would result in a headache.
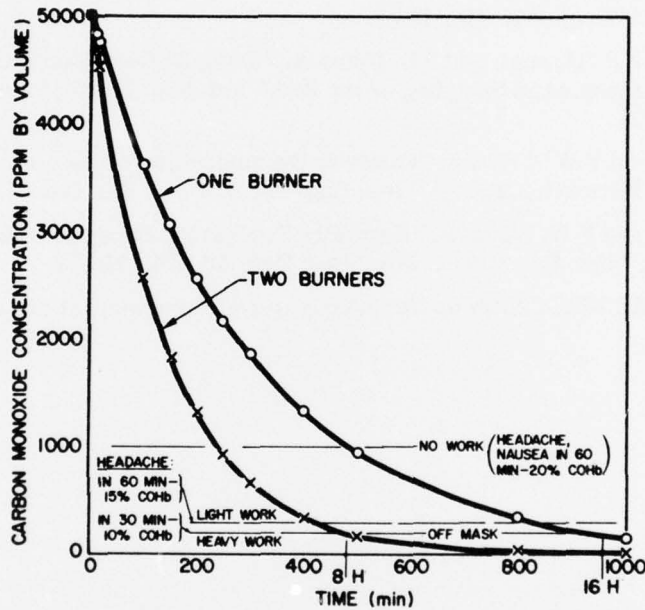
Fig. A1 — Physiological effects at various workloads and CO concentrations

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